

Preparation of Biobased Monofunctional Compatibilizer from Cardanol To Fabricate Polylactide/Starch Blends with Superior Tensile Properties

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ABSTRACT: A biobased monofunctional compatibilizer (called Epicard) is first synthesized by the reaction of cardanol with epichlorohydrin as confirmed by Fourier transform infrared and ^1H NMR. Subsequently, biosourced polymers, polylactide (PLA) and starch, are melt-blended by a twin-screw extruder with Epicard. Confirmed by the measurements of contact angle and ^1H nuclear magnetic resonance of the extracted starches from PLA/starch/Epicard blends, the Epicard only possesses a monoepoxy group to mainly react with starch and then increased the hydrophobicity of the starches during the melt-blending process. As a result, an obvious improvement to the interfacial adhesion between starch and PLA is observed by the scanning electron microscopy. Furthermore, the tensile properties of PLA/starch blends are effectively improved with the addition of Epicard. This study suggests a simple but effective material technique by utilizing a novel plant oil modifier to increase interfacial adhesion in fabricating fully biobased PLA/starch blends with superior tensile properties.

■ INTRODUCTION

In recent years, environmental concerns and shortage of petroleum resources have driven the efforts on development and production of biodegradable and recyclable materials, which are known as “green materials”, to solve disposal problems.^{1–3} Among biodegradable polymers, polylactide (PLA) is a promising polymer with high biodegradability, recyclability, and excellent mechanical properties for industrial plastic applications.^{4–6} However, the disadvantage of the high cost of PLA limits its uses for disposal items. Starch, as a common, inexpensive, and environmental friendly biopolymer, is an attractive candidate as an organic stiffness filler for PLA. Development of advanced materials technology to introduce starch into PLA as the formation of fully biobased composite with superior properties is an important research topic and attracts great attention.^{7–9}

With understanding the difference between hydrophilicity of starch and hydrophobicity of PLA, the increase of the compatibility between the two phases is realized as the primary issue to fabricate PLA/starch composite with high mechanical properties. As reported in the literature, use of reactive compatibilizer is the common approach to solve this issue.^{10–12} Reactive compatibilizers, for example, methylenediphenyl diisocyanate (MDI),¹⁰ acyclic acid (AA),¹³ glycidyl methacrylate (GMA),¹⁴ and maleic anhydride (MA),^{15–17} are recognized to produce a direct chemical linkage (as shown in Figure 1) between the two different phases to reduce the interfacial difference between PLA and starch. As a result, the mechanical properties of the blends are effectively improved. In our previous works,^{18–20} plant oils were also used as the nontoxic respective compatibilizer to increase the compatibility between starch and PLA and thus the effective improvement of mechanical properties.

After deep analysis of the difference existing in the hydrophilicity between starch and PLA, it is found that the

difference is mainly affected by their molecular structure. There is a large amount of hydroxyls on starch. But only a small quantity of hydroxyls can be found on PLA. As a result, it very easily leads to an unbalanced reaction with the reactive compatibilizer. Very limited chemical-bonding linkage can be formed between PLA and starch. This result effectively exhibits an important opposite conclusion; that is, there is no direct relation between compatibility and chemical-bonding linkage. No matter how much chemical-bonding linkage is formed between the two components, it does not hinder the increase of compatibility. Another explanation recognizes that the compatibility between PLA and starch is in fact decided by the interfacial adhesion. For instance, hydrophobic compatibilizers (particularly plant oils) mainly react with starch to produce a hydrophobic surface of starch particle. Accordingly, the interfacial adhesion between starch and PLA is enhanced and thus the compatibility is promoted.

To further exhibit the importance of the increase in interfacial adhesion to improve compatibility between starch and PLA, in this work, a nontoxic monofunctional plant oil compatibilizer without the ability to form chemical-bonding linkage is synthesized to use for the increase in interfacial adhesion. Cardanol (from biobased cashew nut shell oil) with *n*-pentadecadienyl phenol structure^{21–23} is chosen to prepare the monofunctional compatibilizer (called Epicard) by the reaction between cardanol and Epichlorohydrin. And then Epicard is induced to be grafted onto the surface of starch in producing a hydrophobic plant oil layer to increase interfacial adhesion with the PLA. The changes in starch are analyzed by ^1H nuclear magnetic resonance (NMR), and the contact angle

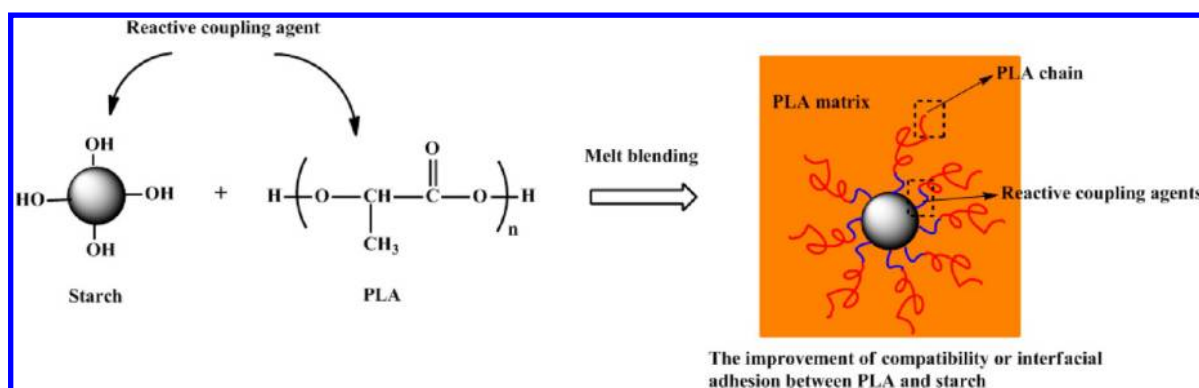


Figure 1. Possible illustration of the increase of the compatibility of PLA/starch composites with the traditional reactive coupling agents during the melt-blending process.

measurements, in detail. The compatibility between starch and PLA is observed by the scanning electron microscopy (SEM). Mechanical properties are also evaluated to show the increase of interfacial adhesion between the two phases of PLA and starch with the addition of Epicard.

EXPERIMENTAL SECTION

Materials. A semicrystalline extrusion grade PLA 4032D is supplied by NatureWorks (Blair, NE, United States). It is vacuum-dried at 80 °C for 8 h prior to use. The native food grade corn starch with the diameter of 5–20 μm is bought from Zhucheng Stimulation Trade and Corn Development Co., Ltd., Shandong, China, which is dried in a vacuum dryer for 24 h at 100 °C before used. Cardanol is obtained from Xuzhou Zhongyan Science and Technology Industrial Co., Ltd., China. Epichlorohydrin (ECH), toluene, and chloroform (CH_3Cl) are from Aladdin Reagent, China. Tetrabutyl ammonium bromide (TBAB) and sodium hydroxide are supplied by Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals are used as received.

Preparation of the Epicard. Twenty grams of cardanol, 45 g of ECH, and 1.6 g of TBAB were placed in a three-necked round-bottomed flask with a magnetic stirrer, a thermometer, and a reflux condenser. After the reactants were mixed vigorously at room temperature for 10 min, it was heated to about 105 °C and maintained at this temperature for another 3 h under nitrogen flow. Then the mixture was cooled to 80 °C. Aqueous solution of sodium hydroxide (113 g; 48 wt %) was added drop by drop into the mixture. After that, the reaction was kept at 50 °C for 3 h before it was washed with deionized water five times. About 60 g of monofunctional epoxide (namely, Epicard) was obtained after removing the water and residual ECH on a rotary evaporator. The epoxy value of the Epicard determined by hydrochloric acid-acetone method was about 0.27. The synthetic process is shown in Figure 2.

Preparation of the PLA/Starch Composites. PLA/starch blends with and without the Epicard were first melt-blended in a screw extruder (Brabender, Germany). The rotation rate and the mixing temperature were set at 40 rpm and 170 °C/175 °C/180 °C/175 °C/175 °C, respectively. Whereafter, the melting blends were water-cooled and sent to a LQ-25 granulator (Hengxi Machinery Manufacturing Co., Ltd., Taizhou, China) to make pellets. Lastly, the pellets of the binary composites were dried at 85 °C in a vacuum-drying oven for 24 h before injection molding.

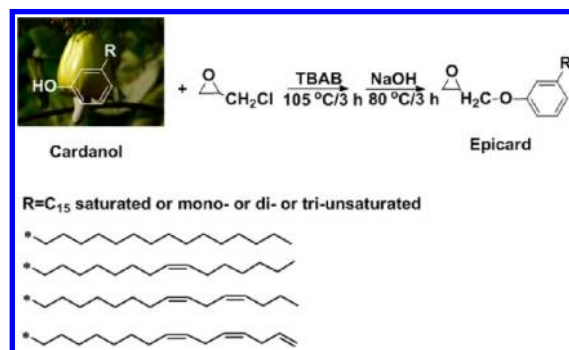


Figure 2. Synthetic route to Epicard.

Extracted Starch from the Composites. To characterize the interfacial state of starch and PLA, the starch fillers from the blends of PLA/starch (70/30), PLA/starch/cardanol (68/30/2), PLA/starch/Epicard (68/30/2), and PLA/starch/Epicard (65/30/5) were first extracted by Soxhlet extraction with methylene chloride for at least 3 days to remove unbonded monomers. The resulting extractants were called Extra-ST, Extra-STC1, Extra-STEC1, and Extra-STEC2. The extracted fillers were vacuum-dried for 5 h at 50 °C.

Characterizations. The structure of the Epicard was analyzed by the Fourier transform infrared (FT-IR) spectrum and ^1H NMR. The infrared spectrum (FT-IR) was recorded with NICOLET 6700 FT-IR (Thermo Fisher Scientific, Waltham, MA, USA). ^1H NMR was performed on a 400 MHz AVANCE III Bruker NMR spectrometer (Bruker, Switzerland) with $\text{DMSO}-d_6$ as a solvent.

Microstructure of the fracture surfaces of PLA/starch composites with the dimensions of 80 \times 10 \times 4 mm were observed by a low expansion scanning electron microscope (SEM, Hitachi TM-1000).

The static contact angles with water and diiodomethane at equilibrium were measured by an OCA 20 contact angle system (Dataphysics Instruments, Filderstadt, Germany), which was equipped with a camera with a precision of $\pm 0.1^\circ$. Six points at least of each sample were recorded and averaged to determine the contact angles, subsequently calculating the dispersive and polar components of the surface energy according to the equations proposed by Wu.²⁴ The surface tension of materials was calculated by eqs 1 and 2:

$$(1 + \cos \theta_{\text{H}_2\text{O}}) \gamma_{\text{H}_2\text{O}} = 4 \left(\frac{\gamma_{\text{H}_2\text{O}}^{\text{d}} \gamma^{\text{d}}}{\gamma_{\text{H}_2\text{O}}^{\text{d}} + \gamma^{\text{d}}} + \frac{\gamma_{\text{H}_2\text{O}}^{\text{p}} \gamma^{\text{p}}}{\gamma_{\text{H}_2\text{O}}^{\text{p}} + \gamma^{\text{p}}} \right) \quad (1)$$

$$(1 + \cos \theta_{\text{CH}_2\text{I}_2}) \gamma_{\text{CH}_2\text{I}_2} = 4 \left(\frac{\gamma_{\text{CH}_2\text{I}_2}^{\text{d}} \gamma^{\text{d}}}{\gamma_{\text{CH}_2\text{I}_2}^{\text{d}} + \gamma^{\text{d}}} + \frac{\gamma_{\text{CH}_2\text{I}_2}^{\text{p}} \gamma^{\text{p}}}{\gamma_{\text{CH}_2\text{I}_2}^{\text{p}} + \gamma^{\text{p}}} \right) \quad (2)$$

where γ is the surface tension, γ^{d} is the dispersion component, γ^{p} is the polar component, and θ is the contact angle with water or diiodomethane.

According to GB/T 1040.1-2006 (China), the samples were injection-molded into 1A type dumbbell-shaped samples with a thickness of 4.0 mm in a HTF90W1 for tensile-testing injection-molding machine (Haitian Plastics Machinery, Ningbo, China). The tensile testing was carried out at a rate of 20 mm/min based on GB/T 1040.1-2006 (China). Four samples for each blend were tested. These samples were located at room temperature for a period of 1 week prior to testing.

On the basis of the standard of ISO179-1:98 (USA), the samples were injection-molded into a type of rectangular solid with a dimension of 80 × 10 × 4 mm for impact testing in a HTF90W1 injection-molding machine (Haitian Plastics Machinery, Ningbo, China). To conduct the impact test, the samples were then notched on a WAY-240 universal sampling machine (Chengde Kecheng Testing Machine Co., Ltd., China); the depth of notch on these samples was arranged from 1.9 to 2.1 mm. The finally notch impact test was performed on a mechanical impact tester (XJ-50Z, Chengde Dahua Testing Machine Co. Ltd., Chengde, China). During the notch impact test, a 2.75 J pendulum was used to determine the notch impact strength. These samples were located at room temperature for a period of 1 week prior to testing, and five samples for each blend were tested.

RESULTS AND DISCUSSION

Characterization of the Epicard. Figure 3 shows the FT-IR spectra of cardanol and synthesized Epicard. The bands at 1046 cm^{-1} are assigned to the characteristic peak of symmetrical and asymmetric C–O–C ring stretching, which indicates the presence of oxirane ring in the Epicard.²⁵

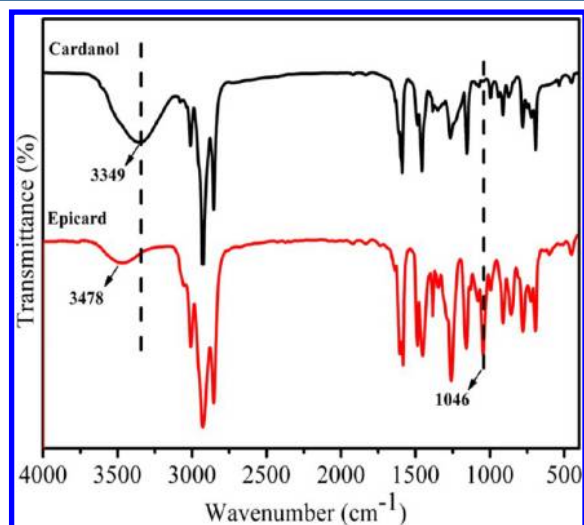


Figure 3. Infrared spectrum of cardanol and Epicard.

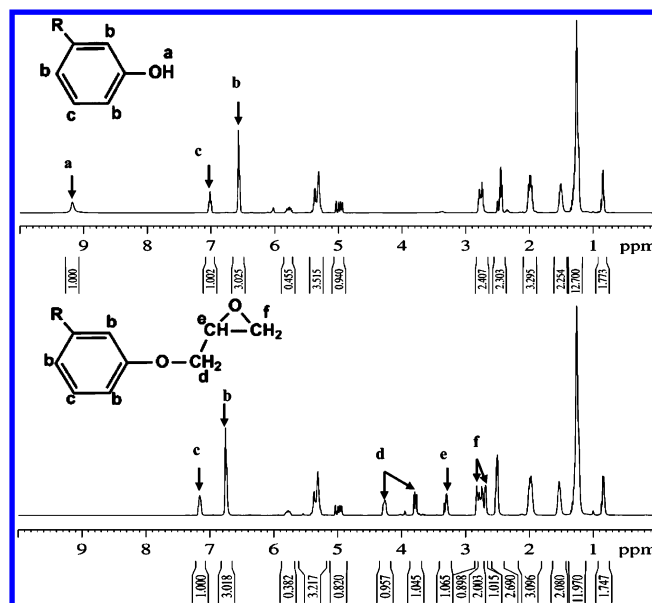


Figure 4. ^1H NMR spectra of cardanol and Epicard.

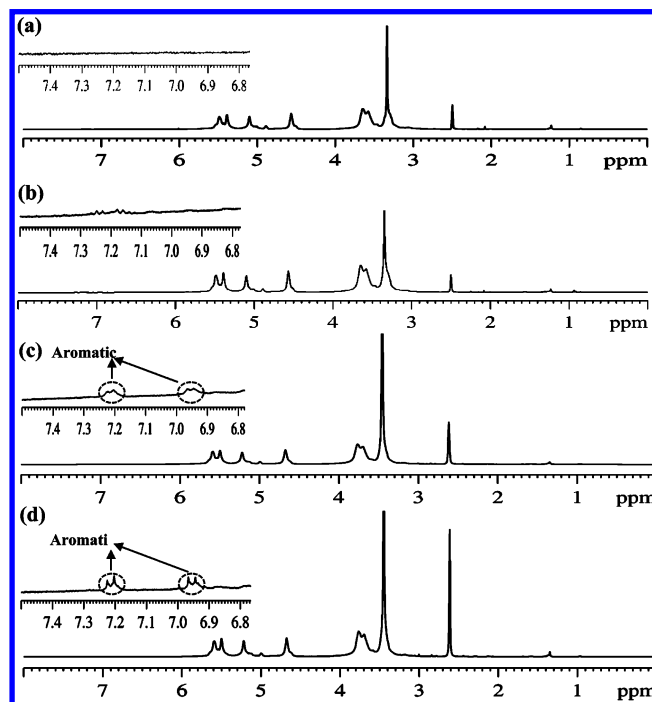


Figure 5. ^1H NMR spectra of extracted starch particles from PLA/starch (70/30) blend (a), PLA/cardanol/starch (68/2/30) blend (b), PLA/Epicard/starch (68/2/30) blend (c), and PLA/Epicard/starch (65/5/30) blend (d).

Meanwhile, the intensity of the band at 3349 cm^{-1} corresponding to the phenolic hydroxyl group decreases and shifts to the high wavenumber in Figure 3. It shows that the phenolic hydroxyl group in cardanol had converted into epoxy group. The chemical structure of cardanol and the Epicard is further determined by ^1H NMR. In Figure 4, the peaks at 6.5, 7.0, and 9.2 ppm shows the protons b, c, and a of the cardanol. Besides these peaks, the other peaks of cardanol shown in Figure 4 are from the residual part of cardanol.²⁶ The peaks at 9.2 attributing to the H proton of the phenolic hydroxyl group in the Epicard disappears, whereas the peaks at 4.3, 3.7, 3.3, 2.8,

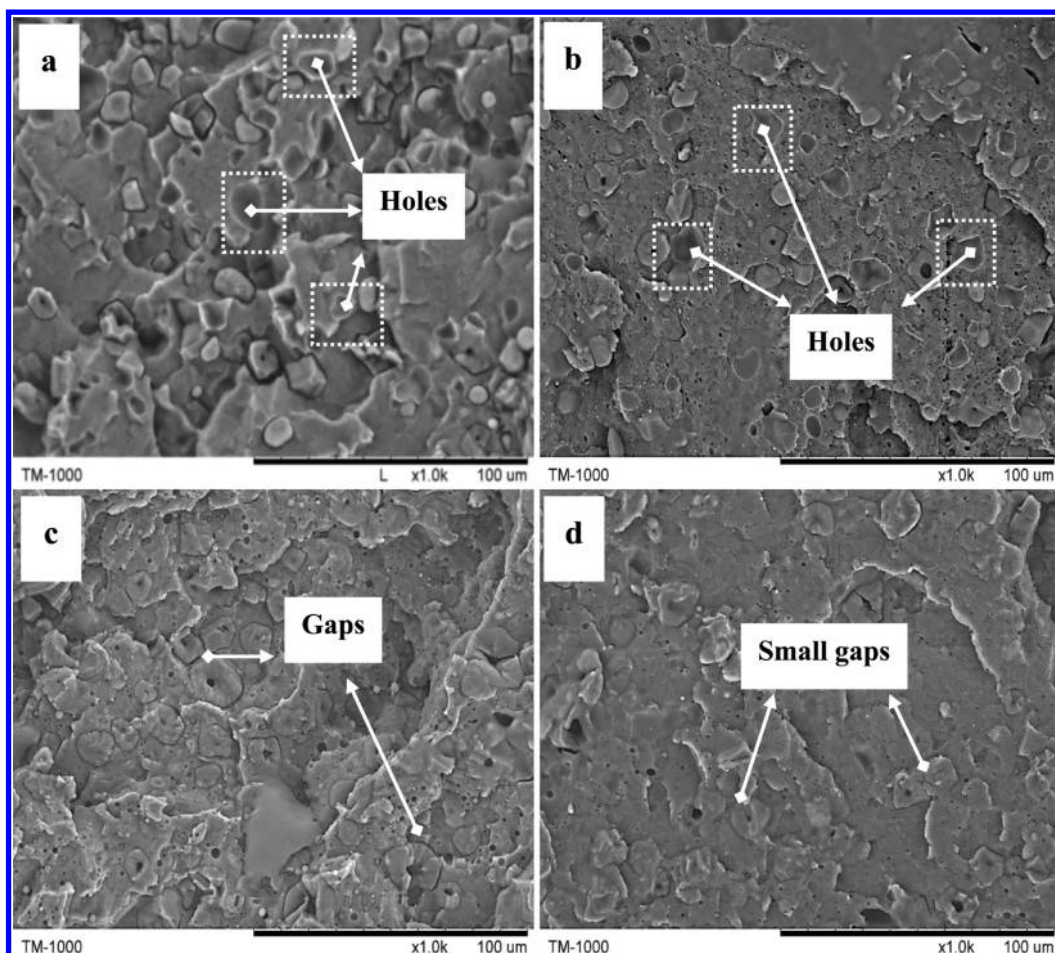


Figure 6. Scanning electron microscopy images of PLA/starch (70/30) blend (a); PLA/cardanol/starch (68/2/30) blend (b); PLA/Epicard/starch (68/2/30) blend (c); and PLA/Epicard/starch (65/5/30) blend (d).

and 2.6 ppm assign to the protons d, e, and f of the epichlorohydrin appearing in Figure 4. All the results indicate the Epicard is successfully produced in the experiment.

Understanding the Effect of the Epicard in PLA/Starch Composites. To reveal the effect of the Epicard in PLA/starch blends, starch is extracted and characterized by ^1H NMR. In Figure 5a,b, no peaks can be found around 6.9–7.2 ppm from ^1H NMR curves of extracted ST and STC1. However, in Figure 5c,d, some peaks at 7.22 and 6.95 ppm attributing to the disubstituted benzene ring of extracted STEC1 and STEC2 appear.²⁷ That is to say, the Epicard has been bonded to the surface of starch particles via the chemical reaction during melt processing. As a result, the starch particles have been encapsulated with the hydrophobic Epicard molecular layer.

Microstructure of PLA/starch blend is also analyzed to show the effect of the change of the starch produced by the Epicard on the interfacial adhesion between PLA and starch. In Figure 6a, many holes with sharp edges are observed at the fracture surface under SEM. Because of the typical characteristics of the difference between hydrophilicity of starch and hydrophobicity of PLA,^{10,28} the interfacial adhesion between PLA and starch is poor. So, the starch particles can be easily removed from PLA matrix to form a hole with sharp edges, which exhibits a weak compatibility of PLA/starch blends. With the addition of 2 wt % cardanol, there still exists some obvious holes with sharp edges at the fracture surface (see Figure 6b). This is because no chemical reaction between starch and cardanol was carried out

(see Figure 5b), and as a result, the weak interfacial adhesion between PLA and starch does not change a lot without the change in the starch. Moreover, there were many pores which might be produced by the coalescence of cardanol that occurred in the PLA matrix in the PLA/cardanol/starch ternary blend.

However, with the addition of 2 wt % Epicard, starch particles could react with Epicard during the melt blending as confirmed in Figure 5c. The starch particles are well-embedded in the PLA matrix and almost no holes appeared in the PLA matrix (see Figure 6c) with the changing of the starch. Furthermore, with the amount of the Epicard increasing up to 5 wt %, only many small gaps between starch and PLA are observed in Figure 6d. There still exists a small amount of unreacted Epicard. The coalescence of the Epicard in melt processing leads to some pores in the composites. Moreover, by use of 5 wt % Epicard in PLA/starch blends (as shown in Figure 7), with the starch amount increasing from 30 to 60 wt %, starch particles are also well-embedded in the PLA matrix. This result exhibits the strong ability of the Epicard to significantly improve the interfacial adhesion between PLA and starch via the reaction between starch and Epicard. With the increase of starch, more and more Epicard reacts with starch. The effect of coalescence is also reduced. As a result, no obvious pores are shown in the SEM image of the PLA/Epicard/starch composite (see Figure 7d).

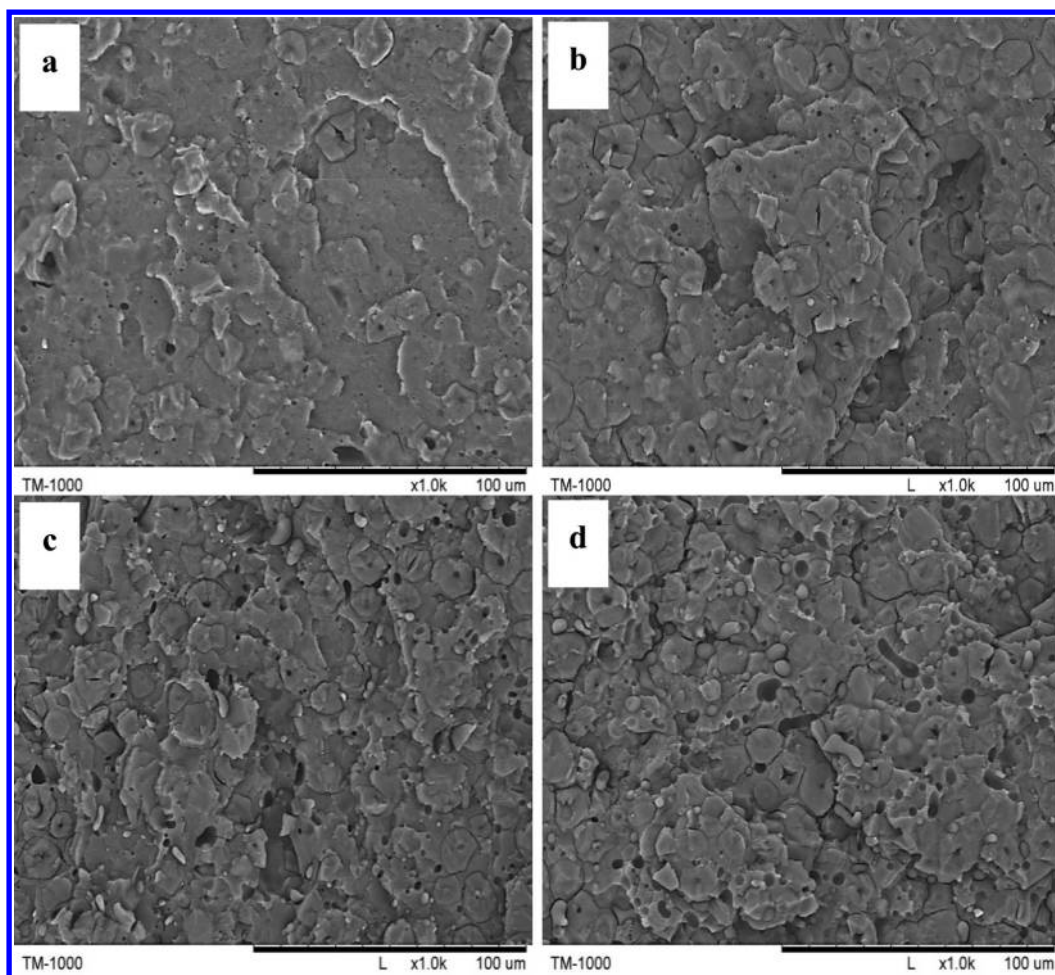


Figure 7. Scanning electron microscopy images of PLA/Epicard/starch (65/5/30) blend (a); PLA/Epicard/starch (55/5/40) blend (b); PLA/Epicard/starch (45/5/50) blend (c); and PLA/Epicard/starch (45/5/60) blend (d).

Table 1. Contact Angle and Surface Tension of the Extracted Starch

samples	contact angle (deg)		surface tension (mN/m)		
	water	diiodomethane	total (γ)	dispersion component (γ^d)	polar component (γ^p)
Extra-ST	44	23	67	43	25
Extra-STC1	50	30	63	42	21
Extra-STEC1	107	40	41	40	1
Extra-STEC2	113	42	33	33	0

Summary of the Effect of Epicard on PLA/Starch Composites. Contact angles of extracted starch are tested with water and diiodomethane to further evaluate the effect on the improvement of interfacial adhesion. Surface tension, dispersion, and polar components of materials are calculated by eqs 1 and 2²⁴ (see Table 1). For the extracted starch particles, because of the reaction between Epicard and starch, it is observed that the surface tension gradually decreased with the increase of the hydrophobicity of extracted starch. Meanwhile, the greater the amount of Epicard used, the lower the surface tension of extracted starch particle, as shown in Table 1. Thus, it is reasonable to believe that by the utilization of the Epicard in the PLA/starch blends, the reaction between starch and

Epicard contributes hydrophobicity to the starch surface (see Table 1) and thus increases the interfacial adhesion between starch and PLA. Moreover, it is well-known that good compatibility in many multicomponent polymer blends, for instance, PLA/poly(3-hydroxybutyrate-co-hydroxycalcerate)/polybutylene succinate,²⁹ Polyamide/monorillonite/rubber,³⁰ and nylon 6/ethylene propylene diene monomer rubber-graft-MA/high-density polyethylene,³¹ has been successfully produced by employing this theory. Therefore, in PLA/starch/Epicard blends, the Epicard essentially serves as an effective reactive compatibilizer. It plays a vital role in significantly increasing the hydrophobicity of starch via a chemical reaction with starch and thus offers a driving force for the improvement of interfacial adhesion or compatibility between PLA and starch, as illustrated in Figure 8.

Mechanical Properties. In this section, besides the change in microstructure and physical properties, mechanical properties of PLA/starch blends are exhibited in detail to analyze the important effect of interfacial adhesion in PLA/starch blends with Epicard. As shown in Table 2, PLA/starch (70/30) composite has poor mechanical properties with tensile strength ~ 33 MPa, elongation $\sim 1.2\%$, and impact strength ~ 2.8 kJ/m². The results indicate low interfacial adhesion between PLA matrix and starch particles for their immiscible characteristics, as shown in Figure 6a. With the addition of 2 wt % cardanol, not much change in mechanical properties is exhibited in Table

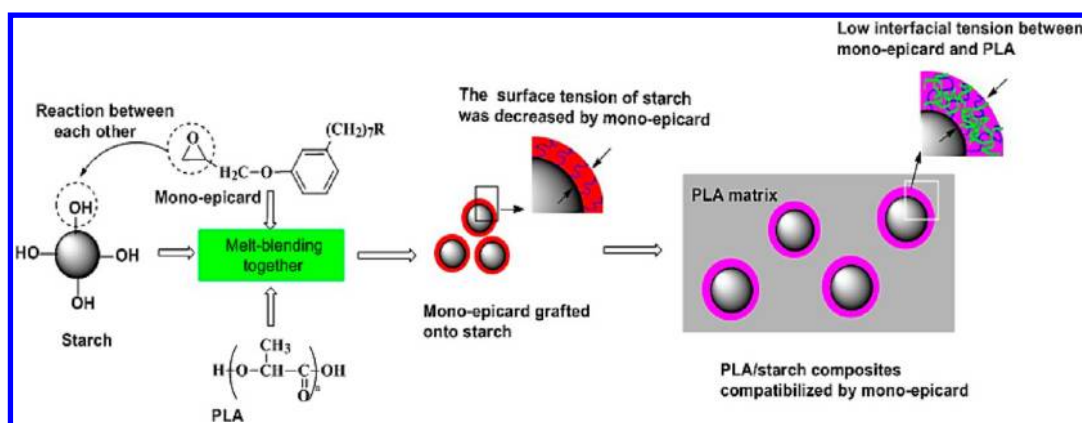


Figure 8. Illustration of the increase of interfacial adhesion and then compatibility between PLA and starch by reaction with Epicard during the melt-blending process.

Table 2. Mechanical Properties of PLA/Starch Blend, PLA/Cardanol/Starch Ternary Blend, and PLA/Epicard/Starch Ternary Blends

samples	tensile modulus (MPa)	tensile strength (MPa)	elongation at break (%)	impact strength (KJ/m ²)
PLA/starch (70/30)	3517 ± 55	33 ± 1	1.2 ± 0.2	2.8 ± 0.1
PLA/cardanol/starch (68/2/30)	3420 ± 62	32 ± 1	1.5 ± 0.2	2.5 ± 0.1
PLA/Epicard/starch (68/2/30)	3690 ± 101	41 ± 2	1.7 ± 0.5	3.3 ± 0.1
PLA/Epicard/starch (65/5/30)	3543 ± 103	46 ± 2	3.3 ± 0.2	4.7 ± 0.5
PLA/Epicard/starch (55/5/40)	3864 ± 76	42 ± 2	2.3 ± 0.1	3.9 ± 0.2
PLA/Epicard/starch (45/5/50)	3969 ± 113	38 ± 1	1.6 ± 0.1	3.1 ± 0.2
PLA/Epicard/starch (35/5/60)	4069 ± 43	35 ± 1	1.3 ± 0.1	2.4 ± 0.1

2. However, after adding 2 wt % Epicard in PLA/starch blends, the tensile strength increases to ~41 MPa. Elongation and impact strength are also improved a little. Furthermore, with the amount of the Epicard increased to 5 wt %, tensile strength, elongation, and impact strength are respectively improved to ~46 MPa, 3.3%, and 4.7 KJ/m². Results show increase of interfacial adhesion produced an obvious increase of mechanical properties. After the content of starch increased up to 60 wt %, the tensile properties of PLA/starch composite with the Epicard could also reach a high level. The tensile strengths, elongations, and impact strengths are also higher than the properties of the composites without using the Epicard.

CONCLUSIONS

In this work, a biobased monofunctional epoxide from cardanol (named as Epicard) is successfully synthesized to serve as an effective reactive compatibilizer to improve the compatibility between PLA and starch via one-step melt blending. The results reveal that Epicard could mainly bond onto the surface of starch via chemical reaction to provide hydrophobicity and then improve the compatibility without any chemical-bonding linkage between PLA and starch. Our current research suggests an effective way to improve interfacial adhesion for the increase of compatibility via monofunctional compatibilizer. With the effective improvement of interfacial adhesion between starch and PLA, a fully biobased PLA/starch blend with superior tensile properties is obtained. This study would provide a novel and simple material technique to design a renewable and effective reactive interfacial modifier in fabricating biobased blends with superior compatibility and tensile properties.

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Notes

The authors declare no competing financial interest.

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